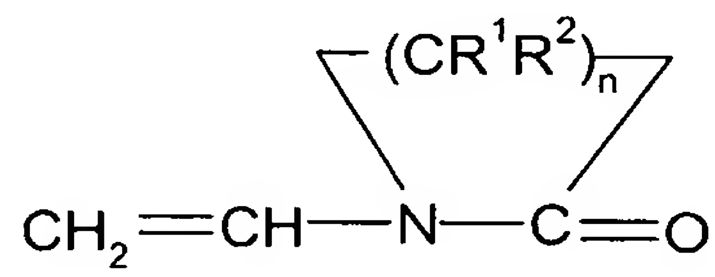
10/591796
IAP12 Rec'd PCT/PTO 06 SEP 2006

Process for preparing aqueous dispersions of polyvinyllactam

Description

The present invention provides a process for preparing a water-in-water dispersion of polyvinyllactam having a K value of ≥ 30 and ≤ 110 by free-radically initiated polymerization of at least one N-vinyllactam of general formula I



(I),

where

R^1 and R^2 independently of one another are hydrogen and/or C_1-C_8 alkyl and
n is an integer from 2 to 8,

in an aqueous reaction medium,
wherein said at least one N-vinyllactam I used for the polymerization is composed of at least 50% by weight of N-vinyl-2-pyrrolidone (R^1 and R^2 as hydrogen, n as 3) and the free-radically initiated polymerization of said at least one N-vinyllactam I takes place in the presence of

a) from 1 to 100% by weight, based on the saturation amount in the aqueous reaction medium, of at least one organic or inorganic salt,
b) from 0.1 to 30% by weight of at least one protective colloid, based on the total amount of said at least one N-vinyllactam I used for the polymerization, and
c) from 0.01 to 3% by weight of at least one free-radical initiator, based on the total amount of said at least one N-vinyllactam I used for the polymerization,

and the reaction conditions are chosen so that during the polymerization reaction at least a portion of said at least one N-vinyllactam I and of the polyvinyllactam formed therefrom by polymerization are present in the form of a separate phase in the aqueous reaction medium.

The present invention further provides the water-in-water dispersion of polyvinyllactam itself and also provides for its use as a component in drug or cosmetic products, in adhesives or heat transfer fluids and also in coating, thickener, adsorber, binder, laundry detergent, plastics, ceramics, refrigerant, ink or pigment formulations. The present invention additionally provides for the use of aforesaid aqueous polyvinyllactam dispersions as a component in a metal quenching bath and, respectively, in adhesive formulations for gluesticks.

The following prior art is a starting point for preparing polyvinyllactam compounds,

especially poly-N-vinyl-2-pyrrolidone (PVP).

WO 91/03496 discloses the solution polymerization by means of tert-amyl peroxypivalate as free-radical initiator. Besides copolymers of maleic anhydride and alkyl vinyl ethers the preparation of PVP having a K value of approximately 120 by polymerization of N-vinyl-2-pyrrolidone (VP) is also described. The PVP content of the high-viscosity aqueous solution disclosed by way of example is approximately 21% by weight.

WO 94/18241 discloses the preparation of PVP having K values in the range from 30 to 150 in the form of high-viscosity aqueous solutions by polymerizing VP using a specific free-radical initiator system composed of at least two free-radical initiators whose 10-hour half-life temperatures differ by more than 5°C.

WO 94/22953 relates to the preparation of PVP having a K value of from 15 to 130 in the form of aqueous solutions by free-radically polymerizing VP or oligomers thereof using as free-radical initiator 2,2'-azobis(2-methylbutanenitrile).

Additionally other processes for preparing PVP having K values $\leq$ 110 by solution polymerization in an aqueous medium have been described and are therefore familiar to the skilled worker (see for example documents US-A 5338814, US-A 5362815, US-A 5373074, RO-A 90406, RO-A93230 and also the American laid-open specification US 2002/22699 A1).

A disadvantage of these processes is that the preparation of these medium to high molecular mass PVP polymers by solution polymerization leads to high viscosities of the PVP solutions, as a function of the target PVP molecular weights, above certain PVP concentrations. The higher the target molecular weight, the lower the polymer content still giving a technically manageable solution viscosity. The poor space/time yields which this entails, particularly in the case of the high molecular mass PVP polymers, result in high production costs. Considered a further disadvantage of the prior art processes are the relatively high fractions of undissolved gel particles, which lead to a multiplicity of disadvantages both in the production operation (longer filtering and dispensing times) and on subsequent application of the PVP polymers (inhomogenieties in the corresponding formulations). A feature of the aqueous PVP solutions generally obtainable by prior art processes that is likewise disadvantageous is that their PVP solids contents are relatively low and that therefore, for use as a formulating component, they must often be blended with pulverulent PVP in order to raise the solids content.

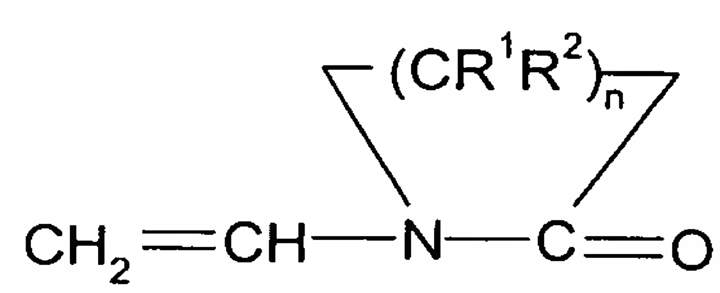
It was an object of the present invention to provide an improved polymerization process for N-vinyllactams, especially N-vinyl-2-pyrrolidone, which exhibits improved

space/time yields and opens up a route to low-viscosity aqueous systems combining higher polyvinyllactam contents with lower gel contents.

The process defined at the outset has been found accordingly.

Processes for preparing water-in-water polymer dispersions by free-radically induced polymerization of ethylenically unsaturated compounds (monomers) are general knowledge (see for example WO 98/31748, WO 98/54234, EP-A 630909, EP-A 984990 or US-A 4380600).

In accordance with the invention at least one N-vinyllactam of general formula I



(I),

where

R^1 and R^2	independently of one another are hydrogen and/or C_1-C_8 alkyl and
n	is an integer from 2 to 8,

are used for the polymerization in an aqueous reaction medium, said at least one N-vinyllactam I being composed of at least 50% by weight of N-vinyl-2-pyrrolidone (R^1 and R^2 as hydrogen, n as 3).

R^1 and R^2 in this formula can independently of one another be hydrogen and/or C_1-C_8 alkyl, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl and also n-pentyl, n-hexyl, n-heptyl or n-octyl and their isomeric alkyl groups. R^1 and R^2 are preferably hydrogen and methyl. Particular preference is given to hydrogen. In many cases the N-vinyllactam I contains no methyl groups or only one in all.

In accordance with the invention n is an integer from 2 to 8, frequently 3, 4, 5, 6 and 7. In particular n is 3 and 5.

Examples of N-vinyllactams I which can be used with advantage in accordance with the invention are the N-vinyl derivatives of the following lactams: 2-pyrrolidone, 2-piperidone, ε-caprolactam and their alkyl derivatives, such as 3-methyl-2-pyrrolidone, 4-methyl-2-pyrrolidone, 5-methyl-2-pyrrolidone, 3-ethyl-2-pyrrolidone, 3-propyl-2-pyrrolidone, 3-butyl-2-pyrrolidone, 3,3-dimethyl-2-pyrrolidone, 3,5-dimethyl-2-pyrrolidone, 5,5-dimethyl-2-pyrrolidone, 3,3,5-trimethyl-2-pyrrolidone, 5-methyl-5-ethyl-2-pyrrolidone, 3,4,5-trimethyl-2-pyrrolidone, 3-methyl-2-piperidone, 4-methyl-2-piperidone, 5-methyl-2-piperidone, 6-methyl-2-piperidone, 6-ethyl-2-piperidone,

3,5-dimethyl-2-piperidone, 4,4-dimethyl-2-piperidone, 3-methyl-ε-caprolactam, 4-methyl-ε-caprolactam, 5-methyl-ε-caprolactam, 6-methyl-ε-caprolactam, 7-methyl-ε-caprolactam, 3-ethyl-ε-caprolactam, 3-propyl-ε-caprolactam, 3-butyl-ε-caprolactam, 3,3-dimethyl-ε-caprolactam or 7,7-dimethyl-ε-caprolactam. It will be appreciated that mixtures of aforementioned N-vinyllactams I can also be used.

Said at least one N-vinyllactam I for polymerization is composed of at least 50% by weight of VP. Often said at least one N-vinyllactam I is composed of ≥ 60%, ≥ 70%, ≥ 80%, ≥ 90% or even 100% by weight, and all values in between, of VP. Frequently VP is used exclusively for the polymerization.

In accordance with the invention the entirety of N-vinyllactam I can be introduced as an initial charge in the reaction medium. It is also possible, however, to introduce only a portion of said at least one N-vinyllactam I as an initial charge in the reaction medium and to supply the remainder if appropriate or the entirety of the N-vinyllactam I to the reaction medium under polymerization conditions.

The process of the invention is conducted in the presence of from 1 to 100% by weight, based on the saturation amount in the aqueous reaction medium, of at least one organic or inorganic salt. The function of said at least one salt is to lower the solubility both of N-vinyllactam I and of the polyvinyllactam formed, so that at least a portion of the N-vinyllactam I used for the polymerization and of the polyvinyllactam formed therefrom by polymerization is present as a separate heterogeneous phase in the aqueous reaction medium under polymerization conditions.

The selection of the salt in question depends essentially on the N-vinyllactam I employed, the polyvinyllactam to be produced, and the protective colloid employed, and also if appropriate further auxiliaries. The selection of the identity and quantity of the salt is made such that under polymerization conditions (temperature, pressure, presence of auxiliaries if appropriate, etc.) not only at least a portion of the N-vinyllactam I used for the polymerization but also at least one portion of the polyvinyllactam formed are present as a separate heterogeneous phase in the salt solution. It is advantageous in accordance with the invention the higher the fraction of N-vinyllactam I and polyvinyllactam present as a separate phase is. It is advantageous if under polymerization conditions ≥ 60%, frequently ≥ 70% and often ≥ 80% by weight of the at least one unreacted N-vinyllactam I and also ≥ 70%, frequently ≥ 80% and often ≥ 90% by weight of the polyvinyllactam formed are present as a separate heterogeneous phase in the aqueous reaction medium.

Salts that can be used for example for the process of the invention are described exhaustively in WO 98/14405 and WO 00/20470, which are hereby incorporated by reference.

Suitable salts are inorganic salts, preferably cosmotropic salts, such as fluorides, chlorides, sulfates, phosphates or hydrogenphosphates of metal ions or ammonium ions. Typical representatives are sodium sulfate, potassium sulfate, ammonium sulfate, magnesium sulfate, aluminum sulfate, sodium chloride, potassium chloride, sodium dihydrogenphosphate, diammonium hydrogenphosphate, dipotassium hydrogenphosphate, calcium phosphate, sodium citrate and iron sulfate.

Chaotropic salts, such as thiocyanates, perchlorates, chlorates, nitrates, bromides and iodides, can likewise be used. Typical representatives are calcium nitrate, sodium nitrate, ammonium nitrate, aluminum nitrate, sodium thiocyanate and sodium iodide.

It is advantageous to use salts of organic C_1 to C_{15} carboxylic acids, especially the alkali metal salts, sodium or potassium salts for example, or ammonium salts of monobasic, dibasic or polybasic organic C_1 to C_{12} carboxylic acids, such as formic acid, acetic acid, citric acid, oxalic acid, malonic acid, succinic acid, adipic acid, suberic acid, phthalic acid, agaricic acid, trimesic acid, 1,2,3-propanetricarboxylic acid and also 1,4-, 2,3- or 2,6-naphthalenedicarboxylic acid, for example.

The aforementioned salts can be used individually or as mixtures of two or more salts. Often a mixture of two or more salts is more effective than one salt alone, based on the amount employed.

The salts are added in an amount which is from 1 to 100% by weight, preferably from 10 to 90% by weight and more preferably from 15 to 75% by weight of the saturation amount in the aqueous reaction medium under reaction conditions.

By 100% by weight saturation amount in the reaction medium is meant the amount of salt or salts which still just dissolves, without precipitating, in the aqueous reaction medium of the employed N-vinyllactam I in the presence of said at least one protective colloid and also if appropriate of further auxiliaries, and at the reaction temperature employed.

In accordance with the invention it is possible for the entirety of said at least one salt to be included in the initial charge in the reaction medium. An alternative possibility is to introduce if appropriate only a portion of said at least one salt as an initial charge in the reaction medium and to supply the remainder if appropriate or the entirety of said at least one salt to the reaction medium under polymerization conditions. In that case, however, it is necessary to ensure that not only the N-vinyllactam I used for the polymerization (up until the time of its reaction) but also the polyvinyllactam formed are always in the form of a separate heterogeneous phase in the aqueous reaction medium under reaction conditions.

The process of the invention takes place in the presence of from 0.1 to 30% by weight, often from 0.5 to 20% by weight and frequently from 1 to 10% by weight of at least one protective colloid, based in each case on the total amount of said at least one N-vinyllactam I used for the polymerization.

A protective colloid for the purposes of this text embraces all compounds whose average molecular weight is > 1000 g/mol, which are readily water-soluble and additionally are capable of stabilizing the droplets of the vinyllactam I, and also in particular of the polyvinyllactam formed, as a heterogeneously disperse phase in the aqueous dispersion medium. Frequently the average molecular weight is from 1500 to 3 000 000 g/mol or from 10 000 to 2 000 000 g/mol and often from 30 000 to 1 500 000, determined in each case by means of standard methods of gel permeation chromatography. Neutral, anionic and/or cationic protective colloids can be used.

For the purposes of this specification an anionic protective colloid refers to all compounds with an average molecular weight > 1000 g/mol whose dispersive molecular structure carries at least one anionic group, such as a sulfonic or carboxylic acid group and also the corresponding salts thereof.

Suitable anionic protective colloids include in particular homopolymers and copolymers of the following monomers: acrylic acid, methacrylic acid, crotonic acid, ethylacrylic acid, itaconic acid, 2-acrylamido-2-methylpropanesulfonic acid, vinylsulfonic acid, vinylsulfuric acid, vinylphosphoric acid, 10-undecenoic acid, 4-pentenoic acid, cinnamic acid, maleic acid, maleic anhydride, fumaric acid, 3-butenoic acid, 5-hexenoic acid, 6-heptenoic acid, 7-octenoic acid, citraconic acid, mesaconic acid, styrenesulfonic acid, styrenesulfuric acid, 3-sulfopropyl acrylate, bis-(3-sulfopropyl) itaconate, 3-sulfopropyl methacrylate, 3-allyloxy-2-hydroxypropane-1-sulfonic acid, 2-acrylamido-2-methyl-ethanesulfonic acid, 2-sulfoethyl acrylate, bis-(2-sulfoethyl) itaconate, 2-sulfoethyl methacrylate, 3-sulfopropyl methacrylate, 3-allyloxy-2-hydroxypropane-1-sulfonic acid, 3-allyloxy-2-hydroxyethane-1-sulfonic acid and also their alkaline metal and ammonium salts, in particular their sodium and potassium salts.

Besides the aforementioned acid-functional monomers the polymeric anionic protective colloids in the form of their copolymers may also include the following neutral monomers in copolymerized form: ethylene, isobutene, N-vinylformamide, VP, N-vinylcaprolactam, N-vinylacetamide, N-vinylcarbazole, vinylaromatic monomers, such as styrene, α-methylstyrene, o-chlorostyrene or vinyltoluenes, vinyl halides, such as vinyl chloride or vinylidene chloride, esters of vinyl alcohol and monocarboxylic acids containing 1 to 18 carbon atoms, such as vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl laurate and vinyl stearate, ethers of vinyl alcohol and monoalcohols containing 1 to 18 carbon atoms, such as methyl vinyl ether for example, esters of

preferably C3 to C6 α,β-monoethylenically unsaturated monocarboxylic and dicarboxylic acids, such as especially acrylic acid, methacrylic acid, maleic acid, fumaric acid and itaconic acid, with generally C1 to C12, preferably C1 to C8 and especially C1 to C4 alkanols, such as particularly methyl, ethyl, n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl and 2-ethylhexyl acrylate and methacrylate, dimethyl or di-n-butyl fumarate and maleate, nitriles of α,β-monoethylenically unsaturated carboxylic acids, such as acrylonitrile, methacrylonitrile, fumaronitrile, maleonitrile, and also C_{4-8} conjugated dienes, such as 1,3-butadiene (butadiene) and isoprene. The aforementioned monomers generally form, in the polymeric anionic protective colloids, the auxiliary monomers which, based on the total monomer amount, account for a fraction of less than 80%, frequently less than 50% and preferably less than 30% by weight. The polymeric anionic protective colloids frequently contain none of the aforementioned monomers in copolymerized form.

For the purposes of this specification a cationic protective colloid is a reference to any compounds having an average molecular weight > 1000 g/mol whose dispersive molecular structure carries at least one cationic group, such as a protonated or alkylated nitrogen-containing group.

Suitable cationic protective colloids include, in particular, homo- and copolymers of the following monomers that are alkylated or protonated on the nitrogen: 1-vinylimidazole, 2-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-methylpyridine, dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, dialkylaminoalkyl acrylamides, dialkylaminoalkyl methacrylamides, 3-aminopropyl vinyl ether, vinylamines or allylamines. Alkylation takes place by methods known to the skilled worker, such as by reaction with dimethyl sulfate, diethyl sulfate or methyl chloride. It will be appreciated that it is also possible to carry out the alkylation by means of aforementioned reagents at the polymer stage.

Besides the aforementioned monomers alkylated or protonated on the nitrogen it is possible for the polymeric cationic protective colloids, in the form of their copolymers, to include aforementioned neutral monomers as well in copolymerized form. In the cationic protective colloids the neutral monomers generally form the auxiliary monomers which, based on the total monomer amount, account for a fraction of less than 80%, frequently less than 50% and preferably less than 30% by weight. In many cases the polymeric cationic protective colloids contain no neutral monomers in copolymerized form.

It will be appreciated that it is also possible for the polymeric protective colloids to contain not only sulfonic and/or carboxylic acid groups but also groups alkylated and/or protonated on the nitrogen. Where the polymeric protective colloids contain more sulfonic acid and/or carboxylic acid groups than groups alkylated and/or protonated on

the nitrogen, they are to be considered as anionic polymeric protective colloids. Where, however, the polymeric protective colloids contain more groups alkylated and/or protonated on the nitrogen than sulfonic acid and/or carboxylic acid groups, they are to be considered as cationic polymeric protective colloids.

Neutral protective colloids contain neither sulfonic acid or carboxylic acid groups nor functional groups alkylated or protonated on a nitrogen atom. Examples of neutral protective colloids include polyvinyl alcohols, polyalkylene glycols, cellulose derivatives, starch derivatives or gelatin derivatives, and also polyvinylformamide, PVP, polyacrylamide, polymethacrylamide, polyhydroxyalkyl acrylate and polyhydroxyalkyl methacrylate.

Neutral, anionic and/or cationic protective colloids are known in principle to the skilled worker. An exhaustive description of suitable protective colloids is given in Houben-Weyl, Methoden der organischen Chemie, volume XIV/1, Makromolekulare Stoffe, Georg-Thieme-Verlag, Stuttgart, 1961, pages 411 to 420.

The weight-average molecular weights of the polymeric protective colloids are preferably in the range from 20 000 to 1 500 000 g/mol, frequently in the range from 30 000 to 1 000 000 g/mol and often in the range from 40 000 to 700 000 g/mol, determined in each case by means of standard methods of gel permeation chromatography.

It is important that the protective colloids are completely soluble in the aqueous reaction medium under reaction conditions in the quantity range actually employed, namely from 0.1 to 30% by weight, based on the total amount of said at least one N-vinyllactam I used for the polymerization, and are able to stabilize the droplets of N-vinyllactam that are present as a dispersely separate phase, and in particular the polyvinyllactam droplets formed.

It is further of importance that the anionic or cationic protective colloids can be used optionally also in combination with neutral protective colloids. The weight fraction of neutral protective colloids used optionally is, however, generally lower than the weight fraction of cationic and/or anionic protective colloids and is often $\leq$ 5% by weight, $\leq$ 3% by weight or $\leq$ 1% by weight, based in each case on the total amount of said at least one N-vinyllactam I used for the polymerization.

Preference is given to using anionic or cationic polymeric protective colloids.

In accordance with the invention the entirety of said at least one protective colloid can be introduced as an initial charge in the reaction medium. An alternative possibility is to include if appropriate only a portion of said at least one protective colloid in the initial

charge in the reaction medium and to supply the remainder, if appropriate, or the entirety of said at least one protective colloid to the reaction medium during the polymerization under polymerization conditions.

As initiators for the free-radical polymerization it is possible to use water-soluble and water-insoluble peroxo compounds and/or azo compounds that are familiar to the skilled worker, such as, for example, alkali metal or ammonium peroxodisulfates, hydrogen peroxide, dibenzoyl peroxide, tert-butyl perpivalate, 2,2'-azobis(2,4-dimethyl-valeronitrile), tert-butyl peroxyneodecanoate, tert-butyl per-2-ethylhexanoate, di-tert-butyl peroxide, tert-butyl hydroperoxide, azobisisobutyronitrile, azobis(2-amidino-propane) dihydrochloride, 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50 from Wako Chemicals GmbH, Neuss) or 2,2'-azobis(2-methylbutyronitrile). Also suitable are free-radical initiator mixtures or redox initiators, such as ascorbic acid/iron(II) sulfate/sodium peroxodisulfate, tert-butyl hydroperoxide/sodium disulfite or tert-butyl hydroperoxide/sodium hydroxymethanesulfonate, for example. The amount of said at least one free-radical initiator is from 0.01 to 3, frequently from 0.05 to 1.5 and often from 0.05 to 1% by weight, based in each case on the total amount of said at least one N-vinyllactam I used for the polymerization.

Through the concomitant use of redox coinitiators, examples of which include benzoin, dimethylaniline and organically soluble complexes and salts of heavy metals, such as copper, cobalt, manganese, nickel and chromium or especially iron, it is possible to lower the half-lives of the stated peroxides, especially the hydroperoxides, so that, for example, tert-butyl hydroperoxide is active even at 100°C in the presence of 5 ppm of copper(II) acetylacetonate.

Preference is given to using readily water-soluble azo initiators, such as 2,2'-azobis-(2-methylpropionamidine) dihydrochloride, for example.

The polymerization reaction is triggered by means of polymerization initiators which break down into free radicals. It is possible to employ all of the initiators known for polymerizing the N-vinyllactams I. Suitable examples include initiators which break down into free radicals and which at the temperatures chosen in each case possess half-lives of less than 3 hours. If the polymerization is conducted at different temperatures, by first initially polymerizing the N-vinyllactams I at a relatively low temperature and then completing polymerization at a significantly higher temperature, then it is advantageous to use at least two different initiators which possess a sufficient dissociation rate in the temperature range chosen in each case.

The polymerization is usually conducted at temperatures between 20 and 100°C, preferably between 30 and 95°C or 50 and 90°C. Frequently the polymerization reaction takes place under atmospheric pressure (1 bar absolute) or, if the

polymerization is conducted in a closed system, under the autogenous pressure. In general the polymerization reaction takes place in the absence of oxygen, under a nitrogen atmosphere for example.

To prepare the aqueous polyvinyllactam dispersions of the invention it is often advantageous, when using anionic polymeric dispersants, for the amount of free-radical initiator to be from $\geq$ 0.01 to $\leq$ 3% by weight and for the polymerization temperature to be in the range from > 70 to $\leq$ 95°C, often in the range $\geq$ 75 to $\leq$ 90°C, while in the polymerization temperature range from $\geq$ 40 to $\leq$ 70°C, or in the range $\geq$ 50 to $\leq$ 65°C, the amount of free-radical initiator is from $\geq$ 0.3 to $\leq$ 3% by weight, based in each case on the total amount of the N-vinyllactam I. When using cationic polymeric dispersants the amount of free-radical initiator in the entire temperature range from $\geq$ 40 to $\leq$ 100°C, preferably in the range $\geq$ 50 to $\leq$ 85°C, is from $\geq$ 0.01 to $\leq$ 3% by weight, often from $\geq$ 0.05 to $\leq$ 1.5% by weight and frequently from $\geq$ 0.1 to $\leq$ 1% by weight, based in each case on the total amount of the N-vinyllactam I.

The polymerization can if appropriate also be conducted in the presence of molecular weight regulators, in order to tailor the molecular weight of the polymers. Examples of suitable polymerization regulators include 2-mercaptoethanols, mercaptopropanols, mercaptobutanols, thioglycolic acid, N-dodecyl mercaptan, tert-dodecyl mercaptan, thiophenol, mercaptopropionic acid, isopropanol, allyl alcohol and acetaldehyde. The molecular weight regulators are used in an amount, based on the vinyllactams I employed, of from 0 to 10, or from 0.1 to 5% by weight, or from 0.1 to 2%, by weight. Molecular weight regulators are frequently employed in the preparation of polyvinyllactams having a K value < 60. The nature and amount of any molecular weight regulators to be used are familiar to the skilled worker or can be determined by said worker in simple preliminary experiments.

The process of the invention is frequently conducted in the presence of buffer substances, which are intended to suppress the hydrolysis of the N-vinyllactams I, especially at a pH < 6. Examples of buffer substances used include sodium bicarbonate and sodium pyrophosphate, and also further compounds familiar to the skilled worker. Their amount, based on the aqueous reaction medium, is frequently from 0.01 to 2% by weight.

The pH of the aqueous reaction medium is generally in the range from 6 to 11, preference nevertheless being given to a pH $\geq$ 6.5 and $\leq$ 10 (measured in each case at 20 to 25 °C).

The aqueous reaction medium may additionally comprise further customary auxiliaries, such as biocides, viscosity regulators or defoamers, for example.

The process of the invention generally takes place such that the polymerization is carried out using ≥ 20% by weight, often ≥ 30% by weight and frequently ≥ 40% by weight and often ≥ 50% by weight of said at least one N-vinyllactam I, based on the total amount of the resulting aqueous polyvinyllactam dispersion.

It is essential that the entirety of said at least one N-vinyllactam I is polymerized in the process of the invention to a conversion of ≥ 90% by weight, often ≥ 95% by weight or frequently ≥ 98% by weight.

The process of the invention can take place either in accordance with the batch technique, with the entirety of said at least one N-vinyllactam I introduced at the beginning, or by the feed technique.

If the polymerization takes place in batch mode, all of the components except for the free-radical initiator are introduced into the polymerization reactor at the start. Subsequently the aqueous polymerization mixture is heated to polymerization temperature, with stirring, and thereafter the free-radical initiator is added, continuously or discontinuously.

In one preferred embodiment the process of the invention is carried out by means of a feed technique. In that case some or all of the reaction components are metered in whole or in part, in steps or continuously, together or in separate feed streams, into the aqueous reaction medium.

Advantageously at least one portion of said at least one organic or inorganic salt and of said at least one protective colloid and also if appropriate a portion of said at least one free-radical initiator and/or of said at least one N-vinyllactam I are introduced as an initial charge in the aqueous reaction medium, with stirring, and under polymerization conditions the remainders if appropriate of said at least one organic or inorganic salt and of said at least one protective colloid and also the entirety or remainder if appropriate of said at least one free-radical initiator and/or of said at least one N-vinyllactam I are metered in discontinuously or, preferably, continuously.

Following the polymerization operation the water-in-water dispersions obtained in the polymerization can be subjected to a physical or chemical aftertreatment.

For this purpose, for example, 0.05 to 1.5% the polymerization is completed by metering additionally from by weight, frequently 0.1 to 1% the polymerization is completed by metering additionally from by weight and often 0.2 to 0.8% by weight, based on the total amount of said at least one N-vinyllactam I used for the polymerization, of at least one of the aforementioned free-radical initiators continuously or discontinuously into the polymerization mixture under polymerization conditions.

Advantageously, the entirety of the free-radical initiator is added discontinuously, in one lot, to the polymerization mixture under polymerization conditions in order to complete the polymerization.

Frequently the polymerization reaction proper is followed by aftertreatment of the resultant water-in-water dispersion by means of steam and/or nitrogen stripping for the purpose of removing highly volatile organic constituents. Methods of steam and/or nitrogen stripping are familiar to the skilled worker.

The water-in-water dispersions obtained are usually milky white and have a viscosity at 25°C of from 5 to 90 000 mPas, often from 10 to 60 000 mPas and often from 15 to 30 000 mPas, measured in each case by the Brookfield method, spindle 4, 10 revolutions per minute.

The polyvinyllactams available through the process of the invention have K values ≥ 30 and ≤ 110, measured by the method of Fikentscher. The weight-average molecular weights of the polyvinyllactams available in accordance with the invention are situated within the range from 15 000 to 3 000 000 g/mol, frequently in the range from 25 000 to 2 800 000 g/mol and often in the range from 30 000 to 2 400 000 g/mol, determined in each case by means of standard methods of gel permeation chromatography.

By K values are meant, for the purposes of this text, generally the values measured by the method of Fikentscher, Cellulosechemie, Vol. 13, pages 58 to 64 (1932) at 25°C in 5% strength by weight aqueous sodium chloride solution. The concentration of the polyvinyllactam under measurement in aforementioned sodium chloride solution is in each case 0.1 part by weight [g] per 100 parts by volume [ml] of 5% strength by weight aqueous sodium chloride solution.

The aqueous polyvinyllactam dispersions available in accordance with the invention can be placed directly on the market. An alternative possibility is for these dispersions to be freed from possibly disruptive accompanying components by means of oxidizing or reducing reagents, adsorption methods, such as the adsorption of impurities on selected media, such as on activated carbon, or by means of ultrafiltration methods. The aqueous polyvinyllactam dispersions available in accordance with the invention can alternatively again be converted into the corresponding polyvinyllactam powders by means of suitable drying methods, such as spray drying, freeze drying or roll drying, with the use of if appropriate of suitable auxiliaries, such as spray drying assistants or anticaking agents, for example.

It is important that the process of the invention opens up a route to aqueous polyvinyllactam dispersions whose polyvinyllactam content, for a given viscosity and given K values of the polyvinyllactam, is above the polyvinyllactam content of aqueous

polyvinyllactam solutions obtainable by solution polymerization. In the case of the aqueous polyvinyllactam dispersions obtainable in accordance with the invention it is frequently possible to obtain a polyvinyllactam content which, for a given viscosity and given K values of the polyvinyllactam, is $\geq$ 2%, $\geq$ 3%, $\geq$ 4%, $\geq$ 5%, $\geq$ 7%, $\geq$ 10% or $\geq$ 15% by weight above the polyvinyllactam content of the polyvinyllactam solution obtainable by solution polymerization. By means of the process of the invention, moreover, better commixing of the lower-viscosity polymerization medium and in unison therewith a higher N-vinyllactam conversion rate, and also better removal of the heat of polymerization per unit time, are achieved. Additionally the polyvinyllactams obtainable by the process of the invention have a lower polydispersity (Mw/Mn) as compared with the polyvinyllactams obtainable via solution polymerization, for given polyvinyllactam contents.

It is significant that the polyvinyllactams available in accordance with the invention can be used with advantage, in the form of their water-in-water dispersions or in the form of their polymer powders, as a component in drug or cosmetic products, in adhesives, heat transfer fluids, in coating, thickener, adsorber, binder, laundry detergent, plastics, ceramics, refrigerant, ink or pigment formulations and also in metal quenching baths. The aqueous polyvinyllactam dispersions obtainable in accordance with the invention can be employed with particular advantage as components in gluesticks or in metal quenching baths.

The use of polyvinyllactam solutions, especially PVP solutions, as a component in aqueous metal quenching baths is known (see for example publications US-A 3902929, US-A 4528044, US-A 4738731, DE-A 3345253, DE-A 3345254, DE-A 4415098, EP-A 218677 or JP-A 62170415). For the use of PVP in aqueous metal quenching baths it is important that the cooling rates of the quenching baths can be adjusted in a targeted way by adjusting the PVP concentration and the average PVP molecular weight. In this context the skilled worker is familiar with the particular PVP concentration and average PVP molecular weight and/or PVP K value that are particularly suitable for a specific metal cooling problem. Frequently for metal quenching baths use is made of PVP with K values of $\geq$ 30 to $\leq$ 110, in particular with K values of $\geq$ 30, $\geq$ 60 or $\leq$ 90. The PVP concentrations in the aqueous metal quenching baths are often in the range from $\geq$ 1 to $\leq$ 30% by weight, based on the total amount of the metal quenching bath.

Particularly in the context of reformulating the aqueous metal quenching baths and also in connection with the readdition of PVP to used metal quenching baths, use of the low-viscosity but simultaneously highly concentrated aqueous PVP dispersions of the invention simplifies the metering and commixing operation, since the low-viscosity PVP dispersions can be added in finely metered form and can easily be distributed homogeneously. Contact with the PVP solution already present or, in the case of

reformulation of the metal quenching bath, with water, automatically results, through dilution effects, in a PVP solution of higher viscosity with homogeneous PVP distribution.

The preparation of solid adhesive formulations for gluesticks is another application to which the aqueous polyvinyllactam dispersions obtainable in accordance with the invention, especially the PVP dispersions, are very well suited. The use of PVP in adhesive formulations is known to the skilled worker (see for example publications US-A 3576776, US-A 4750482, US-A 5338814 or WO 98/47953). Frequently PVP is used with K values of ≥ 30 to ≤ 110, often of ≥ 60 to ≤ 100 or of ≥ 75 to ≤ 95 for producing gluesticks.

The gluestick formulations are prepared by subjecting the individual components, especially water, humectant, gelling agent, the adhesive itself, and also customary auxiliaries, examples being white pigment (titanium dioxide), odorants, antioxidants, preservatives, etc., for example, to homogeneous mixing. The amount of PVP as adhesive is generally between 20% and 40% by weight, based on the total amount of the adhesive formulation. Aqueous PVP solutions are often used for preparing the adhesive formulations. Particularly in the case of adhesive formulations with high PVP contents in conjunction with high PVP K values, however, the PVP contents of the PVP solutions obtainable by solution polymerization, limited in PVP content owing to the solution viscosity, are no longer sufficient for that purpose, however. In these cases a frequent remedy is to prepare the adhesive formulation using not only an aqueous PVP solution but also PVP powders, which are obtainable by means of energy-intensive and hence cost-intensive drying operations, in particular a spray drying or freeze drying operation, of the aqueous PVP solutions, with identical or different K value. A problem in this context, however, is that the homogeneous incorporation of the PVP powder into the adhesive formulation, owing to the very high viscosities, presents difficulties from the standpoint of apparatus and, furthermore, is very time-consuming.

Particularly advantageous adhesive formulations are those comprising an aqueous polyvinyllactam dispersion having a polyvinyllactam solids content $\geq 25\%$ by weight with a K value of the polyvinyllactam of ≥ 60 to ≤ 100.

An adhesive formulation typical for gluesticks is frequently composed of

20 to 40% by weight of	PVP and if appropriate further adhesive components,
20 to 70% by weight of	deionized water,
5 to 15% by weight of	gelling agents,
2 to 15% by weight of	humectants, and
0 to 15% by weight of	further additives, such as color pigments, antioxidants, odorants or preservatives, for example

Through use of the highly concentrated aqueous PVP dispersions obtainable in accordance with the invention it is possible, when preparing adhesive formulations, to do without the use of aqueous PVP solutions and PVP powders, obtainable for example from the PVP solutions by a drying operation, such as a spray drying or freeze drying operation, and to dispense with the blending thereof, thereby simplifying the production operation.

The process of the invention allows access to highly concentrated water-in-water dispersions of polyvinyllactams having K values $\geq$ 30 and $\leq$ 110 with good space/time yields. These dispersions, in spite of their high polyvinyllactam content, are of low viscosity and additionally have a negligibly small gel content, if any at all. The aqueous polyvinyllactam dispersions can be put to diverse uses. Particularly when these aqueous dispersions are used as a formulating ingredient it is possible to incorporate high quantities of polyvinyllactam into the formulations without having to perform cost-intensive blending of aqueous polyvinyllactam solutions with pulverulent polyvinyllactam.

The examples which follow are intended to illustrate the invention, though without restricting it.

Examples

Analysis

Determination of the Fikentscher K value was made at 25°C by means of a 5% strength by weight solution of sodium chloride in deionized water, using an instrument from Schott, Mainz (capillary: Micro-Ostwald; type: MO-Ic). The aqueous polyvinyllactam dispersion and the 5% strength by weight aqueous sodium chloride solution were mixed so that the resulting homogeneous solution had a polyvinyllactam content of 0.1 g per 100 ml of 5% strength by weight aqueous sodium chloride solution.

The polyvinyllactam content of the aqueous polyvinyllactam dispersion was determined by drying an aliquot thereof to constant weight in a drying oven at 140°C. The polyvinyllactam content is calculated from the corrected dry residue, based on the aliquot of aqueous polyvinyllactam dispersion used for drying. The corrected dry residue is the dry residue obtained after drying, minus the auxiliaries present alongside the polyvinyllactam in the aliquot of the aqueous polyvinyllactam dispersion used for drying, such as the amount of free-radical initiator and the amount of protective colloid, organic or inorganic salts, and other auxiliaries if appropriate.

The viscosity of the aqueous polyvinyllactam dispersion obtained was determined in accordance with ISO 2555 at 25°C using a Brookfield instrument, model DV-II with spindle 4 at a rotary speed of 10 revolutions per minute.

Example 1

A 1.5 l polymerization reactor with anchor stirrer was charged at 20 to 25°C (room temperature) with

431 g	of deionized water
80 g	of sodium sulfate (anhydrous, Merck, Darmstadt)
177 g	of a 22.5% strength by weight aqueous solution of a copolymer (of acrylic acid and vinylformamide in a 3:7 quantitative ratio, with subsequent hydrolysis of the formamide groups and neutralization of the carboxylic acid groups by means of aqueous sodium hydroxide solution, with a weight-average molecular weight of about 300 000 g/mol [polymeric dispersant A]).

Subsequently the pH of this reaction mixture was adjusted to 6.8 using a 5% strength by weight aqueous solution of sulfuric acid and thereafter this reaction mixture was heated with stirring (160 rpm) to 60°C under a nitrogen atmosphere. After 60°C had been reached, 10% by weight of the feed streams I and II, described below, were added to the reaction mixture, with stirring and retention of the reaction temperature,

and the system was stirred for 5 minutes under the abovementioned conditions.

Thereafter the remainders of feed streams I and II were metered in over the course of two hours, beginning simultaneously and with constant feed stream flows, into the reaction mixture, with stirring and retention of the reaction temperature. After the end of feed streams I and II polymerization was continued at 60°C for three hours more.

Subsequently the reaction mixture was heated to 75°C. Thereafter feed stream III was added all at once to this polymerization mixture, which was left at this temperature with stirring for a further two hours. Subsequently the polymer dispersion was cooled to room temperature.

Feed stream I:

320 g	of N-vinyl-2-pyrrolidone (from BASF AG, Ludwigshafen)

Feed stream II was an aqueous solution composed of:

0.5 g	of 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50, from Wako Chemicals GmbH, Neuss)
47.5 g	of deionized water

Feed stream III was an aqueous solution composed of:

1 g	of V-50
9 g	of deionized water

The K value of the PVP obtained was found to be 77, the viscosity of the resultant aqueous dispersion 1.5 Pas and the PVP content of the aqueous dispersion 30% by weight.

Example 2

Example 2 was prepared as for Example 1 but using the following raw materials and amounts thereof:

Initial charge:

421 g	of deionized water
91.2 g	of trisodium citrate dihydrate (Fluka AG, Germany)
177 g	of a polymeric dispersant A

Feed stream I:

320 g	of N-vinyl-2-pyrrolidone

Feed stream II was an aqueous solution composed of:

0.5 g	of V-50
47.5 g	of deionized water

Feed stream III was an aqueous solution composed of:

1 g	of V-50
9 g	of deionized water

The K value of the PVP obtained was found to be 84, the viscosity of the resultant aqueous dispersion 9.8 Pas and the PVP content of the aqueous dispersion 30.1% by weight.

Example 3

Example 3 was prepared as for Example 1 but using the following raw materials and amounts thereof:

Initial charge:

376 g	of deionized water
76.9 g	of trisodium citrate dihydrate
95.9 g	of a 35.1% strength by weight aqueous solution of a copolymer (of maleic anhydride and methyl vinyl ether in a 1:1 quantitative ratio, with subsequent complete hydrolysis of the anhydride groups and neutralization by means of aqueous sodium hydroxide solution, with a K value of 90 and a weight-average molecular weight of about 160 000 g/mol)

Feed stream I:

270 g	of N-vinyl-2-pyrrolidone

Feed stream II was an aqueous solution composed of:

0.9 g	of V-50
64.5 g	of deionized water

Feed stream III was an aqueous solution composed of:

0.8 g	of V-50
15 g	of deionized water

The K value of the PVP obtained was found to be 91, the viscosity of the resultant aqueous dispersion 4 Pas and the PVP content of the aqueous dispersion 30.1% by weight.

Example 4

Example 4 was prepared as for Example 1 but using the following raw materials and amounts thereof and conducting polymerization and postpolymerization at 80°C:

Initial charge:

383 g	of deionized water
76.9 g	of trisodium citrate dihydrate
89.1 g	of a 37.8% strength by weight aqueous solution of a polyacrylic acid neutralized with aqueous sodium hydroxide solution, with a K value of 80 and a weight-average molecular weight of about 100 000 g/mol [polymeric dispersant B])

Feed stream I:

270 g	of N-vinyl-2-pyrrolidone

Feed stream II was an aqueous solution composed of:

0.4 g	of V-50
64.5 g	of deionized water

Feed stream III was an aqueous solution composed of:

0.8 g	of V-50
15 g	of deionized water

The K value of the PVP obtained was found to be 96.7, the viscosity of the resultant aqueous dispersion 4.2 Pas and the PVP content of the aqueous dispersion 30.3% by weight.

Example 5

Example 5 was prepared as for Example 1 but using the following raw materials and amounts thereof:

Initial charge:

282 g	of deionized water
91.9 g	of trisodium citrate dihydrate
142 g	of a polymeric dispersant B

Feed stream I:

430 g	of N-vinyl-2-pyrrolidone

Feed stream II was an aqueous solution composed of:

1.3 g	of V-50
102 g	of deionized water

Feed stream III was an aqueous solution composed of:

1.3 g	of V-50
25 g	of deionized water

The K value of the PVP obtained was found to be 96, the viscosity of the resultant aqueous dispersion 88 Pas and the PVP content of the aqueous dispersion 40.1% by weight.

Example 6

Example 6 was prepared as for Example 1 but using the following raw materials and amounts thereof (the entirety of feed stream I was included in the initial charge):

Initial charge:

450 g	of deionized water
91.2 g	of trisodium citrate dihydrate
177 g	of a polymeric dispersant A
320 g	of N-vinyl-2-pyrrolidone

Feed stream II was an aqueous solution composed of:

1.0 g	of V-50
8.6 g	of deionized water,

which was metered in within 10 seconds.

Feed stream III was an aqueous solution composed of:

1.9 g	of V-50
17.3 g	of deionized water

The K value of the PVP obtained was found to be 82, the viscosity of the resultant aqueous dispersion 16 Pas and the PVP content of the aqueous dispersion 30.1% by weight.

Comparative example

The comparative example was prepared as for Example 1 but without using sodium sulfate.

The experiment had to be abandoned after the addition of about 210 g of N-vinyl-2-pyrrolidone, owing to the resultant excessive viscosity.